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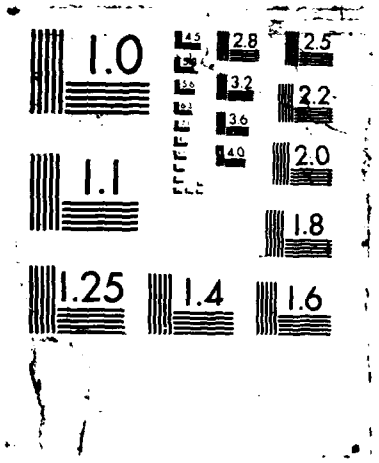
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The pentacoordinate phosphorus (V) hydride cyclenphosphorane has been treated with a variety of transition metal carbonyls. The first examples of σ^3,σ^1-metallo-bis(methylene) phosphoranes and metal-free phosphorus (V) hydrides have been produced. Unstable aryl-substituted metaphosphate moieties, $ArOPO_2^-$, have been produced in the gas phase. Phosphavinylidenes have been found to undergo both facile electrophilic and nucleophilic attack. The synthetic usefulness of phosphaalkynes has also been explored.

(organic phosphorus compounds)

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REACTIONS OF ORGANOMETALLIC COMPOUNDS WITH PHOSPHORUS (V) ESTERS AND RELATED SPECIES

FINAL TECHNICAL REPORT

ALAN H. COWLEY

NOVEMBER 30, 1987

U. S. ARMY RESEARCH OFFICE

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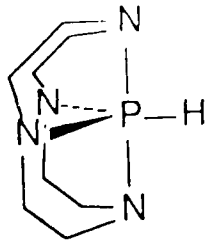
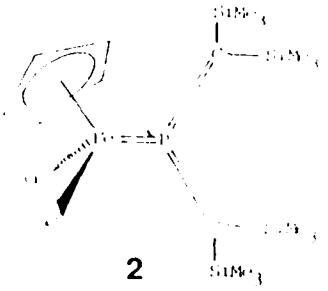
The pentacoordinate phosphorus (v) hydride, cyclenphosphorane (cyclenPH) reacts



CyclenPH

with transition-metal carbonyl dimers such as $Co_2(CO)_8$ to yield a covalent complex, (cyclenP)$Co(CO)_3$ and a salt, [cyclenPH_2] [$Co(CO)_4$][1]. Similarly, cyclenPH reacts with [$Mo(\eta\text{-}C_5H_5)(CO)_3]_2$ to yield (cyclenP)$Mo(\eta\text{-}C_5H_5)(CO)_2$ and [cyclenPH_2] [$Mo(\eta\text{-}C_5H_5)(CO)_3$]. The only isolable product from the reaction of cyclenPH with $Mn_2(CO)_{10}$ is the salt [CyclenPH_2] [$Mn(CO)_5$]. No reaction was observed between cyclenPH and $[Fe(\eta\text{-}C_5H_5)(CO)_2]_2$. All of the metal carbonyl salts are stable in THF solution except for [cyclenPH_2] [$Co(CO)_4$] which loses H_2 and CO upon heating to afford (cyclenP)$Co(CO)_3$. The ligand cyclenPH also reacts with $HW(\eta\text{-}C_5H_5)(CO)_3$ to yield the salt [cyclenPH_2] [$W(\eta\text{-}C_5H_5)(CO)_3$]. The addition of CH_3I to [cyclenPH_2] [$W(\eta\text{-}C_5H_5)(CO)_3$] produces [cyclenP$H_2$]I and $CH_3W(\eta\text{-}C_5H_5(CO)_3$. The X-ray structure of (cyclenP)$Mo(\eta\text{-}C_5H_5)(CO)_2$ reveals that the phosphorus atom adopts a distorted trigonal bipyramidal geometry in which the Mo atom occupies an equatorial site. The P-Mo-N triangle causes severe distortion in the bond lengths of the cyclenP moiety, and one of the axial P-N bond lengths is extremely long (1.852(2)Å).

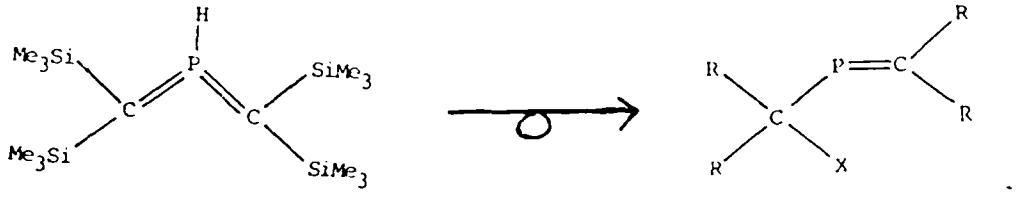
The bis-methylenephosphorane $ClP[=C(SiMe_3)_2]_2$ reacts with $[\eta^5\text{–}C_5H_5)Fe(CO)_2]K$ to afford **2**, the first example of a λ^3-metallo-bis(methylene) phosphorane [2].



2

Unfortunately, it has not been possible to grow crystals of **2** suitable for X-ray diffraction study. However, the proposed structure is fully consistent with spectroscopic data. For example, NMR data are in accord with existence of **R** and **S** stereoisomers. One interesting feature of the ^{31}P NMR data is the fact that the chemical shift of **2** is 220 ppm upfield of that of $ClP[=C(SiMe_3)_2]_2$. This observation is attributed to a donor-acceptor interaction between the a" HOMO of the $C_5H_5\ Fe(CO)_2$ fragment and the vacant phosphorus $3p_z$ orbital.

The first example of a metal-free three-coordinate phosphorus (v) hydride, **3**,



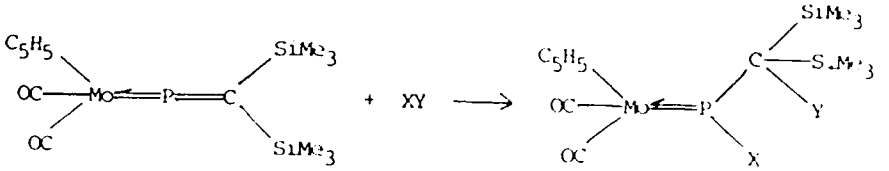
3 **4**

has been prepared by the treatment of $ClP[=C(SiMe_3)_2]_2$ with i-PrMgCl in Et_2O[3]. It is presumed that the reaction proceeds via a β-hydride abstraction from an isopropyl methyl group of $i\text{-}PrP[C(SiMe_3)_2]_2$. Interestingly, it is not possible to prepare **3** by conventional reduction methodology. Heating **3** slightly above the melting point (44-46°C) results in quantitative conversion to the phosphaalkene, **4** via a 1,2 reductive hydride shift. This rearrangement is attributed to the fact that the P-H bond enthalpy is approximately 100KJ mol^{-1} less than that of the C-H bond.

Unstable aryl-substituted metaphosphate moieties, $ArOPO_2$, have been produced in the gas phase by flash vaccum pyrolysis of 2-aryloxy-1,3,2- dioxaphospholanes [4]. The metaphosphates rearrange to cyclic phosphonic monoesters via intramolecular

insertion reactions unless an abstractable β-hydrogen is present and Chugaev-type reactions take place to give terminal alkenes.

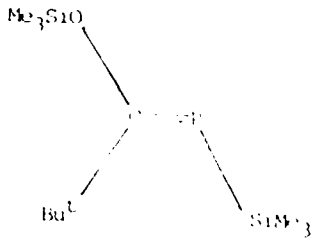
The observation that the phosphorus atom of phosphavinylidenes, $L_nM{=}P{=}CR_2$, is double bonded to both carbon and a transition metal stimulated our interest in the reactivity of this class of compound, special emphasis being placed on the production of phosphite ester complexes. Indeed, it has been found that phosphavinylidene **5** reacts rapidly and quantitatively with EtOH to afford the corresponding three-electron donor terminal phosphido complex (X=EtO, Y=H)[5].



5

Other electrophiles react virtually quantitatively with **5** e.g. X-Y= MeO-H, i-Pr_2N-H, and C_6F_5S-H. Treatment of **5** with an excess of MeOH results in production of the phosphite complex, [η-C_5H_5)$(CO)_2$(H)MoP$(OCH_3)_2$CH$(SiMe_3)_2$]. The reaction of **5** with the nucleophiles Me^- or H^-, followed by treatment with MeOH or MeI, affords [(η-C_5H_5)$(CO)_2$MoC$(SiMe_3)_2$ PR_1R_2] (R_1,R_2=H, Me)[6]. The reaction of **5** with MeO^- is more complex and appears to involve an equilibrium between cyclic and acyclic anions.

Nitriles have proved to be extremely useful synthons for organic synthesis. It is only more recently, however, that the synthetic potential of the corresponding phosphaakynes, RC≡P, has begun to be appreciated. The bulky arylated phosphaalkyne, (2,4,6-t-$Bu_3C_6H_2$)C≡P (**6**) has been prepared by treatment of (2,4,6-t-$Bu_3C_6H_2$)C(O)Cl with Li[P$(SiMe_3)_2$][7]. The isolation of **6** in crystalline form permitted the first X-ray crystallographic measurement of the phosphorus-carbon triple-bond length (1.516(13)Å). Our work with **6** caused us to re-investigate the reaction of t-BuC(O)Cl with Li[P$(SiMe_3)_2$]. Conducting this reaction at 78°C results in the exclusive formation of isomer 7E[8].

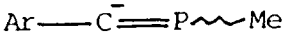


7E

7Z

On the other hand, **7Z** is formed in virtually quantative yield if the reaction is carried out at [illegible]. There is no evidence for the interconversion of **7E** and **7Z** either thermally or photochemically. As expected, the reactivities of these isomers are remarkably different. For example, **7Z** decomposes via $(Me_3Si)_2O$ elimination to afford the desired phosphaalkyne, t-BuC≡P, while **7E** undergoes t-BuSiMe$_3$ elimination. Of particular interest is the fact that in the presence of small quantities of molecular oxygen, hydrocarbon solutions of **7E** are converted into t-BuC≡P in quantitative yields. Both **7E** and **7Z** produce high yields of the phosphaalkyne upon treatment with stoichiometric quantities of $Fe_2(CO)_9$.

The reactions of **6** with several nucleophiles have been explored. For example, reaction of **6** with an equimolar quantity of MeLi results in the carbanion **8**, while the use of an excess of the phosphaalkyne produces the dimeric carbanion, **9**.



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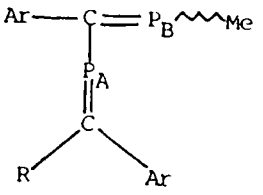

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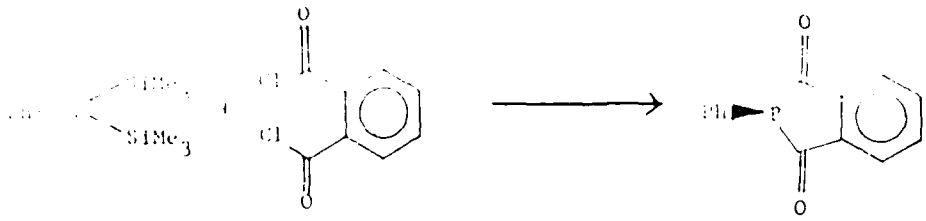
Both **8** and **9** react with alkyl halides to form the corresponding phosphaalkenes and 1,3 diphosphabutadienes. This work represents a new approach to the synthesis of these classes of compounds.

Cyclic carboxylic monoimides find extensive use as polymer precursors, fungicides, herbicides, and pharmaceuticals. Interestingly, prior to our work the corresponding phosphorus heterocycles were unknown. Five-,six-, and seven-membered cyclic carboxylic monophosphides have been prepred by treatment of bis(trimethylsilyl) phosphines with acid chlorides as exemplified below for phthaloyl

chloride [9].



Interestingly, this synthetic procedure is not succesful when saturated organic halides are employed. Possibly this implies the necessity for prior coordination of the bis(trimethylsilyl)phosphine followed by Me_3SiCl elimination. The cyclic carboxylic monophosphides are reactive toward a wide variety of electrophiles, including O_2, S_8, I_2, and MeOH. It is also possible to prepare metal complexes by treatment with sixteen-electron fragments such as $Fe(CO)_4$.

Finally, a review of metal phosphinidene chemistry has been written under ARO sponsorship [10]. Structural studies of the cyclic phosphite, [2,4,6-t-$Bu_3C_6H_2POCH_2CH_2O$] and the iron complex, [$(CO)_4FeP(SiMe_3)_3$] have also been carried out [11,12].

List of Publications Arising from Contract DAA 29-84-K-0186

1. M. Lattman, S. K. Chopra, A. H. Cowley, And A. M. Arif, "Reactions of "Cylenphosphorane" with Transition-Metal Carbonyl Dimers and Hydrides: Synthesis of Phosphoranide Adducts and Metal Carbonyl Anions and the X-ray Crystal Structure of (Cyclen)PMoCp$(CO)_2$", Organometallics, 5, 677 (1986).
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3. A. R. Barron and A. H. Cowley, "Synthesis of a Metal-Free Three-Co-ordinate Phosphorus (V) Hydride and Its conversion to a Phospha-alkene via Reductive Hydride Shift", J. Chem. Soc., Chem. Commun., 1092 (1987).
4. J. I. G. Cadogan, A. H. Cowley, I.Gosney, M. Pakulski, P. M. Wright, and S. Yaslak, "Thermally-induced Gas-Phase Phosphonylation of Arenes via Intramolecular Trapping of an Aryl Metaphosphate Moiety", J. Chem.Soc., Chem. Commun., 1685 (1986).
5. A. M. Arif, A. H. Cowley, and S. Quashie", Reactivity of a Phosphavinylidene. Reactions at both Phosphorus-Carbon and Phosphorus-Molybdenum Double Bonds and a New Approach to Three-Electron Donor Phosphido Complexes", J. Chem. Soc., Chem. Commun., 1437 (1986).
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7. A. M. Arif, A. R. Barron, A. H. Cowley, and S. W. Hall, "Reaction of the Phospha-alkyne ArC=P (Ar=2,4,6-$Bu^t_3C_6H_2$) with Nucleophiles: A New Approach to 1,3-Diphosphabutadiene Synthesis", J. Chem. Soc., Chem. Commun. in press.
8. A. R. Barron, A. H. Cowley, and S. W. Hall, "Remarkable Differences in the Reactivities of the E and Z Isomers of a Phospha-alkene", J. Chem. Soc., Chem. Commun., 980 (1987).
9. A. R. Barron, S. W. Hall, and A. H. Cowley "Cyclic Carboxylic Monophosphides: A New Class of Phosphorus Heterocycle", J. Chem. Soc., Chem. Commun., in press.

10. A. R. Barron and A. H. Cowley, "The Quest for Terminal Phosphinidene Complexes", Acc. Chem. Res., in press.

11. A. H. Cowley, M. Pakulski, and N. C. Norman, "Structural Studies on Bulky Phosphines: X-ray Crystal Structures of [2,4,6-$(t\text{-Bu})_3C_6H_2P(SiMe_3)_2$] and [2,4,6-$(t\text{-Bu})_3C_6H_2POCH_2CH_2O$], Polyhedron, 6, 915 (1987).

12. A. R. Barron , A. H. Cowley, and C. M. Nunn, "Structure of Tetracarbonyltris(trimethylsilyl) phosphine Iron (O)", Acta Cryst., in press.

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